Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program
1001 I Street
Sacramento, CA 95812

STUDY 320: Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern California during Fiscal Year 2020–2021

Aniela Burant, Ph.D.
November 2020

1. Introduction

Southern California urban areas have considerable pest pressures, which results in high urban pesticide use. According to the Pesticide Use Report (PUR) over 15,700,000 pounds of pesticides were applied for non-agricultural use in 2017 (CDPR, 2019). Non-agricultural use includes applications for residential, industrial, institutional, structural, or vector control purposes (CDPR, 2014). PUR data do not account for non-professional applications by residents and homeowners, so actual use is higher. Los Angeles, Orange, and San Diego counties, all counties in Southern California, accounted for 22.5% of the total reported non-agricultural use. Specifically, 2,489,130 pounds of pesticides were applied for professional structural pest control or landscape maintenance in Los Angeles, Orange, and San Diego counties in 2017. Urban areas in Southern California are highly developed, with a high percentage of impervious surfaces. Impervious surfaces enhance surface water runoff, which increases the potential for pesticides to enter urban creeks and rivers via storm drains (Gan et al., 2012).

The California Department of Pesticide Regulation's (CDPR) Surface Water Protection Program (SWPP) has been monitoring pesticides in urban waterways since 2008. Study 320 is a continuation of CDPR's urban monitoring in Southern California (Study 270) (Budd, 2018). The work described herein complements Study 299, which monitors for pesticides in urban areas of Northern California (Ensminger, 2019). These studies have shown that urban-use pesticides (e.g., pyrethroids, fipronil, imidacloprid, and synthetic auxin herbicides) are commonly detected in urban waterways (Ensminger et al., 2013a). SWPP is particularly interested in cases where pesticide concentrations repeatedly reach or exceed USEPA Aquatic Life Benchmarks, which are a type of toxicity thresholds used to gauge potential risks to sensitive aquatic organisms (Gan et al., 2012; Oki and Haver, 2009; Weston et al., 2014; Weston et al., 2005; Weston et al., 2009). Numerous urban waterways are listed on the 2016 Federal Clean Water Act Section 303(d) list due to the confirmed presence of pyrethroid and organophosphate pesticides (Cal EPA, 2018). High use, high potential for pesticide runoff to enter urban waterways, and historical exceedances of aquatic life benchmarks justify the need to continue monitoring California's urban waterways.

This study is also designed to evaluate water quality trends that could show changes in pesticide concentrations over time particularly at long-term monitoring sites. CDPR has taken significant mitigation actions to address water quality exceedances for pyrethroids and fipronil in recent years. Surface water regulations (Chapter 3, Sections 6970 and 6972 in the California Code of Regulations) went in effect in July 2012 to address pyrethroid concentrations in California surface waters (CDPR, 2013); and in 2018, new California specific labels were adopted for fipronil-containing products registered for outdoor use. These mitigation actions were designed to reduce loading of pyrethroids and fipronil to surface waters. Long-term monitoring could provide data that allow CDPR to assess improvements in water quality, such as downward trends in pesticide concentrations and/or decreased exceedances of toxicity thresholds.

Previous monitoring efforts have focused on pesticide loading into receiving waters from residential areas; however, there is little known about the relative contribution of pesticides from other land-uses, such as commercial and industrial sites. An exploratory site will be added to the current monitoring protocol to measure pesticide loading from an area draining commercial land use. In addition, the effectiveness of a low cost mitigation strategy will be evaluated under field conditions at two monitoring locations. Specific modifications from the Study 320 Fiscal Year (FY) 19 – 20 sampling plan are presented in Section 4.9.

2. Objectives

The goal of this project is to assess pesticide concentrations found in runoff at drainages and receiving waters within Southern California urbanized areas during rain events and dry season conditions. Specific objectives include:

1) Determine presence and concentrations of selected priority pesticides in runoff and receiving waters of Southern California urban watersheds under dry and storm conditions;
2) Compare measured concentrations of pesticides to aquatic toxicity thresholds;
3) Evaluate pesticide concentration trends through long-term monitoring;
4) Determine the acute toxicity of water samples using laboratory tests conducted with the amphipod *Hyalella azteca* and the midge *Chironomus* species;
5) Monitor deposition of sediment-bound pyrethroids within selected watersheds;
6) Evaluate commercial land-use as potential source of pesticides to urban waterways; and
7) Evaluate effectiveness of carbon filled socks to reduce pesticides in urban runoff under field conditions.

3. Personnel

The study will be conducted by staff from the CDPR's Environmental Monitoring Branch under the general direction of Jennifer Teerlink, Environmental Protection Manager I. Key personnel are listed below:

Project Leader: Aniela Burant, Ph.D.
Field Coordinator: Jason Carter, Ph.D.
Reviewing Scientist: Robert Budd, Ph.D.

Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program
1001 I Street
Sacramento, CA 95812
Laboratory Liaison: Christopher Collins
Analytical Chemistry: Center for Analytical Chemistry, Department of Food and Agriculture (CDFA)

Collaborators: University of California - Cooperative Extension Orange County – South Coast Research and Extension Center, Los Angeles Public Works, Los Angeles Sanitation District, City of San Diego, County of San Diego, and Orange County Public Works.

Please direct questions regarding this study to Aniela Burant, Senior Environmental Scientist (Specialist), at (916) 445-2799 or Aniela.Burant@cdpr.ca.gov.

4. Study Plan

4.1 Site Selection

The sites described in this protocol, with the exception of the exploratory site, have been previously sampled by CDPR (Burant, 2019; Budd, 2018). These sites were selected using the watershed prioritization component of the Surface Water Monitoring Prioritization (SWMP) Model. The SWMP model, which is extensively described in Luo, et al. (2017), identifies priority hydrologic-unit codes (HUC) based on reported pesticide use and toxicity data. Using the SWMP Model and its aggregation tool (Luo, et al., 2017), the top ten priority HUC8s are identified for Southern California (Appendix 1). Of these, SWPP currently has monitoring sites within six of the top HUC8s. These watersheds, located throughout heavily urbanized areas of Southern California, provide data to evaluate the spatial distribution of priority pesticides in Southern California surface waters (Budd et al., 2013; Luo et al., 2013). Other factors such as site accessibility, contributing land use, perennial flow, other monitoring agency representation, and budgetary constraints direct site selection in the remaining HUCs.

4.1.1 Los Angeles County

Ballona Creek (BAL), Bouquet Canyon Creek (BOQ), Los Angeles River (LAR), San Gabriel River (SGR), Compton Creek 1 (CC1), and Dominguez Channel (DC) are the watersheds of interest in Los Angeles County (Figure 1). All sites are located within concrete-lined channels. These sites are large watersheds with mixed residential and commercial land-use. BAL is in the Santa Monica Bay HUC8 and drains mostly residential land-uses with single- and multi- family homes. BOQ consists of predominantly affluent single-family homes with a small amount of commercial land-use. Although not in a HUC8 identified by the SWMP Model, BOQ has historically high pesticide detections. CC1, a new site in FY19-20, is included again in FY20-21's sampling plan. CC1 is in the Los Angeles River HUC8 was chosen for its contributing land use characteristics. CC1 has a high percentage of residential land-use. LAR1, in the Los Angeles River HUC8, drains residential land-uses, but has a higher percentage of commercial and industrial land-uses than BAL or BOQ. Two exploratory storm drain sites along the LA River (LAR3 and LAR4) were included in last year's study to determine relative contributions from commercial-dominated land-use sites. These sites drain from downtown Los Angeles. These sites will be included in FY 20-21. DC has the highest percentage of commercial and industrial land-uses of the any of the receiving waters in this study. SGR consists primarily of wastewater effluent during low flows. Both DC and SGR are in the San Gabriel HUC8.

4.1.2 Orange County

Ambient water quality monitoring will be conducted at six sampling locations within Salt Creek (SC, Figure 2), three locations within Wood Creek Canyon (WC, Figure 3), one site in the Anaheim-Barber City Channel, and one site along Bolsa Chica Channel (ABCC and BCC, Figure 4) in Orange County. ABCC was misidentified as Bolsa Chica Channel (BCC) in FY 18-19; these are the same sampling sites. A sampling site along BCC was included in last year's sampling plan, just upstream of the confluence of BCC and ABCC. An exploratory storm drain site along Peters Canyon Channel, will be added to this year's sampling plan.

Sampling stations within Salt Creek (SC1, SC2, SC3, SC4, SC5, and SC7) have been monitored consistently since 2009 as part of CDPR's urban monitoring program. The surrounding drainage areas within the Salt Creek watershed consist of single-family dwellings, multiple-family dwellings, light commercial buildings, parks, schools, and two golf courses. SC1–SC4 are located directly below storm drains that receive runoff from residential neighborhoods. SC5 and SC7 are located at the receiving waters of urban inputs and will allow evaluation of pesticide concentrations in the watershed as well as downstream transport of pesticides. All SC sites are located in the Aliso-San Onofre HUC8.

Monitoring locations within Wood Creek, all located in the Aliso-San Onofre HUC8, have been monitored since 2009 as part of SWPP's mitigation evaluation monitoring in urban settings. The monitoring sites are situated at the inlet (WC1) and outlet (WC2) of a small (~0.18 acres) constructed wetland designed to reduce pollutants in urban runoff (Budd, et al., 2012). The wetland receives urban runoff from a drainage area consisting entirely of single- and multiple-family residential units. The primary objective of monitoring at these stations is to observe the efficacy of pesticide removal within the wetland system. Efficacy will be evaluated through comparisons in average pesticide concentrations between the inlet and outlet. A second storm drain (WC3), located within the Wood Creek Watershed, will be monitored for pyrethroids only.

Sampling along the Anaheim-Barber City Channel, which is concrete-lined, and the Bolsa Chica Channel, which has a sediment streambed, will continue. Both watersheds are mixed residential, commercial, and industrial area. The watersheds are located within the Seal Beach HUC8, the highest priority HUC8 in Southern California based on estimated urban pesticide use within the delineated HUC.

An exploratory site in Orange County will be added to the sampling plan this year. The inclusion of an exploratory site to determine relative contributions from commercial-dominated land-use sites is currently under consideration for long-term monitoring. A storm drain along Peters Canyon Channel, just upstream of the confluence of Peters Canyon Channel and San Diego Creek, will be included. This site is located in the Newport Bay HUC8 and upstream of a site monitored by the State Water Resources Control Board's Stream Pollution Trends (SPoT) Monitoring Program. This site, San Diego Creek at Alton Parkway, has historic detections of pyrethroids in sediment (SWAMP, 2017).

Two socks (1 biochar, 1 activated carbon filled) will be placed at the outfalls of two storm drains in Orange County. Effectiveness of this treatment technology will be measured by comparing pre- and post-carbon sock pesticide concentrations. Implementation will occur in the dry-season.

4.1.3 San Diego County

Two stations within the San Diego River watershed, as well as one within the Chollas Creek watershed, will be monitored in San Diego County (Figure 5, Table 1, and Appendix 2). San Diego River and Chollas Creek are not channelized or concrete-lined, which may account for historically lower pesticide concentrations (Budd, 2018). Each of these sites are located within high priority HUC8s in Southern California (Appendix 1). Sampling locations within San Diego County are located near the base of their respective watersheds (i.e., the downstream portion of the watersheds).

4.1.4 Collaborative Monitoring

CDPR has been engaged in a collaborative effort with the State Water Resources Control Board through its SPoT Monitoring Program to increase the data available for trend analysis of current-use pesticides (SWAMP, 2017). The synergistic partnership allows each agency to maximize information gained with limited resources. In coordination with CDPR, the SPoT Program also collects sediments throughout California for pyrethroid and fipronil analyses, which greatly adds to the spatial representation of pesticide monitoring data. Several sites described in this protocol also serve as SPoT monitoring locations for sediments, including BAL, BOQ, LAR1, SGR, and SC5. CDPR collects and analyzes the aqueous samples, while SPoT monitors for pyrethroids and fipronil in sediment. Both sets of data are considered in long-term trend analysis.

4.2 Selection of Pesticides for Monitoring

The SWMP Model was utilized for pesticide selection for ambient monitoring (Budd et al., 2013; Luo et al., 2013). Luo, et al. (2013) describes the SWMP Model in detail, but briefly, the model is based on current pesticide use (PUR, 2016–2018) patterns and aquatic toxicity threshold values. Use data from Los Angeles, Orange, and San Diego counties and aquatic life benchmarks set by the U.S. EPA were considered. The product of the use and toxicity scores yields a final score that represents a relative prioritization of pesticides. In addition, the output generates a monitoring recommendation based on physical-chemical properties such as half-life and solubility. Pesticides that receive a final score of nine or higher are given priority for monitoring. Pesticides with lower scores have either low use in urban environments and/or low associated aquatic toxicity. However, the decision to monitor a pesticide is also influenced by additional factors such as previous monitoring data, budgetary constraints, and analytical capabilities. Thirty-four pesticides received a final score equal to or greater than nine (Appendix 3). These pesticides will be analyzed using five analytical screens: a pyrethroid screen, liquid chromatography (LC) multi-analyte screen, dinitroaniline screen, and phenoxy herbicide screen. Note that the dinitroaniline screen now contains chlorfenapyr, which was previously a one-compound standalone screen. All suites cannot be analyzed at every monitoring location due to budgetary constraints. Priority is given to the pyrethroid and pesticides included in the liquid chromatography (LC) multi-analyte screen. Several sampling locations (SC3, ABCC, BCC, BOQ, SC7, BAL and LAR; depending on the sampling event) will serve as representative watersheds to determine the extent of pesticide concentrations, where all five analytical method screens will be run (Table 2). At these sites, screens that contain pesticides with lower detection frequencies in previous monitoring, such as the dinitroaniline screen, or pesticides that have not previously exceeded benchmarks (e.g., phenoxy herbicides), will be analyzed (Appendix 4).

4.3 Water Sampling

Whole water samples will be collected during two dry-season and two storm sampling events. Dry-season sampling will occur in August 2020 and June 2021. CDPR will attempt to collect storm samples during the first major storm (rain) event of FY 20–21 and during a second major storm in the winter or early spring of 2021 (Table 2).

Dry-season water samples will be collected as grab samples directly into 1-L amber bottles (Bennett, 1997). Where the stream is too shallow to collect water directly into these bottles, a stainless-steel container will be used to initially collect the water samples. Water samples collected during storm events at up to five locations within Salt Creek or Wood Creek watersheds may be collected as time-weighted composite samples utilizing automated sampling equipment set up by UC Cooperative Extension (CDPR, 2011;

Sisneroz et al., 2012). Flow-weighted storm runoff will be collected at BAL, CC1, and LAR1 by the Los Angeles County Public Works Department. Storm runoff composite samples collected at SDR1, SDR4 and CHO1 will be collected by the County and City of San Diego, respectively. Samples will be stored and transported on wet ice or refrigerated at 4°C until analyzed. Field duplicates and/or field blanks will be collected during each sampling event for quality assurance.

4.4 Sediment Sampling

Sediment samples will be collected at three locations (Table 2). Enough sediment will be collected to fill ½ pint Mason jars using stainless-steel scoops from the top of the bed layer, biasing for fine sediments where possible (Mamola, 2005). All sediments will be passed through a 2-mm sieve to remove plant debris and then homogenized (Mamola, 2005). Samples will be analyzed for pyrethroids.

4.5 Toxicity Sampling

Water samples will be collected at a subset of sampling sites for toxicity analysis (Table 3). Grab samples will be collected in 1-L amber I-Chem certified 200 bottles (or equivalent) and transported to the Aquatic Health Program at the University of California, Davis. Toxicity testing will measure percent survival of the amphipod *Hyalella azteca* or the midge *Chironomus sp.* in water over 96-hours (Table 3). Several sites described in this protocol also serve as SPoT monitoring locations for sediment toxicity, including BAL, BOQ, LAR1, SGR, SDR1, PCC1, LAR3, LAR4 and SC5 (depending on the sampling event). Data will be shared between monitoring programs.

4.6 Field Measurements

Physical-chemical properties of water column will be determined using a YSI-EXO 1 multi-parameter Sonde according to the methods describe by Doo and He (2008). At each site, water chemistry parameters measured *in situ* will include pH, temperature, salinity, total dissolved solids, and dissolved oxygen. Storm drain flow rates will be measured to characterize the flow regime and to estimate the total loading of target pesticides. Discrete time flow estimations will be determined using either a Global portable velocity flow probe (Goehring, 2008), utilizing a float or fill-bucket method. Continuous flow rates will be obtained at SC2, SC3, and WC2 using an installed Hach Sigma 950 flow meter (Sisneroz et al., 2012; Oki and Haver, 2009).

4.7 Sample Transport

CDPR staff will transport samples following the procedures outlined in CDPR SOP QAQC004.01 (Jones, 1999). A chain-of-custody record will be completed and accompany each sample.

4.8 Organic Carbon and Suspended Sediment Analyses

CDPR staff will analyze water and sediment samples for total organic carbon (TOC) and dissolved organic carbon (DOC) using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan) (Ensminger, 2013b). Water samples will also be analyzed for suspended sediment (Ensminger, 2013c). Lab blanks and calibration standards will be run before every sample set to ensure the quality of the data.

4.9 Modifications from Study 320 FY 20-21

The current sampling plan is an extension of Study 270 conducted during fiscal years 2009–2019 and Study 320 conducted in FY19-20. Details of the previous year's sampling protocol are described in the document titled "Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern California during Fiscal Year 2019-2020" (Budd, 2018). The sampling and analysis schedule is similar to that for FY 19–20, with a few notable modifications (Table 4), including the addition of an exploratory site to determine pesticide loading from commercial land-use and evaluating the effectiveness of two carbon socks to remove pesticides under field conditions.

5. Chemical Analysis

Pesticide analysis will be conducted by the Center for Analytical Chemistry at the California Department of Food and Agriculture, Sacramento, CA (CDFA). CDFA will analyze five analytical suites (Appendix 4). Sediment samples will be analyzed for pyrethroids (Appendix 4). Laboratory QA/QC will follow CDPR guidelines and will consist of laboratory blanks, matrix spikes, matrix spike duplicates, surrogate spikes, and blind spikes (Segawa, 1995). Laboratory blanks and matrix spikes will be included in each extraction set.

6. Data Analysis

Data generated by this project will be entered into a central database that holds all data including field information, field measurements, and laboratory analytical data. We will use various non-parametric statistical methods to analyze the data. The data collected from this project may be used to develop or calibrate urban pesticide runoff models.

Preliminary analysis (Budd et al., 2020) indicated that the sample data are skewed and contain a number of non-detects with multiple reporting limits, which may violate the normality and equal-variance assumptions of the parametric procedures (e.g., ANOVA and *t*-tests). The application of non-parametric procedures to skewed and censored environmental data is most appropriate for this study (Helsel, 2012). The data will be analyzed by using the R statistical program (R Core Team, 2014), specifically the Non-detects And Data Analysis for environmental data (NADA) package for R (NADA Package for R), and Minitab.

Based on the study objectives, preliminary analysis, and data availability, we propose the following statistical procedures for data analysis (Table 5).

1) Explanatory data analysis will be performed to summarize the characteristics of the sample data. Urban monitoring data have been collected since 2008 for a variety of analytes (Appendix 4) at multiple locations (e.g., Salt Creek, Wood Creek) with different site types (i.e., storm drain outfalls and receiving waters), and between different seasons (i.e., dry and wet seasons) (Tables 1 and 2). Boxplots, histograms, probability plots, and empirical distribution functions will be produced to explore any potential patterns demonstrated by the data.
2) Hypothesis tests will be conducted to compare the concentration between groups of interest. For example, we will test whether there is significant difference in concentration between the dry and wet seasons, or between the different locations. Non-parametric procedures will be used to compute the statistics for hypothesis testing. Data with multiple reporting limits will be censored at the highest limit before proceeding if the test procedure allows only one reporting limit.
3) Trend analysis will be included to demonstrate changes in concentration over time (if any). For the trend analysis, we will use Akritas-Thenil-Sen non-parametric regression, which regresses the censored concentration on time, or the Kaplan-Meier method, which tests the effects of year, month, and location by developing a mixed linear model between the censored concentration and the spatial-temporal factors.

Finally, we will attempt to develop statistical models to assess the factors potentially affecting pesticide concentrations in surface water. We intend to develop a logistic regression model to estimate and predict the likelihood of detection or exceedance of reporting limits or toxicity thresholds. A series of explanatory variables will be examined, including but not limited to: rainfall, field measurements (e.g., flow rate, pH, water TOC, sediment TOC, and TSS), number of households contributing to the storm drain outfall/creek, residential density, percent of impervious areas, season (or month), year, and regulation. Further literature review will be conducted to identify possible explanatory variables in favor of the model.

7. Timeline

Field Sampling: Aug 2020 – Jun 2021
Chemical Analysis: Aug 2020 – Oct 2021
Report to Management: Jan 2022 – Mar 2022
Data Entry into SURF: Mar 2022 – Jun 2022

8. Literature Cited

Bennett, K. 1997. California Department of Pesticide Regulation SOP FSWA002.00: Conducting surface water monitoring for pesticides.

Budd, R., O'Geen, A., Goh, K.S., Bondarenko, S., Gan, J. 2009. Efficacy of Constructed Wetlands in Pesticide Removal from Tailwaters in the Central Valley, California. *Environmental Science and Technology,* 43(8): 2925-2930.

Budd, R., Ensminger, M., Kanawi, W., Goh, K. 2012. A Tale of Two Wetlands: Using Constructed Wetlands to Mitigate Pesticides in Urban Runoff. Department of Pesticide Regulation. Poster presented at SETAC North America Meeting.

Budd, R., Deng, X., Ensminger, M., Starner, K., Luo, Y. 2013. Method for prioritizing urban pesticides for monitoring California's urban surface waters. Department of Pesticide Regulation. Analysis memo.

Budd, R. 2018. Urban monitoring in Southern California watersheds FY 2016-2017. Department of Pesticide Regulation. Study Report.

Budd, R., Wang, D., Ensminger, M., Phillips B. 2020. An evaluation of temporal and spatial trends of pyrethroid concentrations in California surface waters. *Science of the Total Environment*, 718, 137402.

Burant, A. 2019. Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern California during Fiscal Year 2019-2020. Department of Pesticide Regulation, Protocol.

Cal/EPA. 2018. State Water Resources Control Board. The Integrated Report – 303(d) list of water quality limited segments and 305(b) surface water quality assessment.

CDPR. 2011. Department of Pesticide Regulation Standard Agreement No. 10-C0101.

CDPR. 2013. California Code of Regulations. (Title 3. Food and Agriculture) Division 6. Pesticides and Pest Control Operations.

CDPR. 2014. Department of Pesticide Regulation's Agricultural and Non-Agricultural Pest Control Use. Bulletin number ENF-003.

CDPR. 2019. California Department of Pesticide Regulation's Pesticide Information Portal, Pesticide Use Report (PUR) data. Accessed on June 11, 2019.

Doo, S. and L-M. He. 2008. California Department of Pesticide Regulation SOP EQWA010.00: Calibration, field measurement, cleaning, and storage of the YSI 6920 V2-2 multiparameter sonde.

Ensminger, M., Budd, R., Kelley, K., and K. Goh. 2013a. Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of

California, USA, 2008 – 2011. *Environmental Monitoring and Assessment*, 185 (5): 3697-3710.

Ensminger, M. 2013b. Analysis of whole sample suspended sediments in water.

Ensminger, M. 2013c. Water TOC analysis using the Shimadzu TOC-VCSN and ASI-V Autosampler.

Ensminger, M. 2017. Ambient Monitoring in Urban Areas in Northern California for FY 2016-2017. Department of Pesticide Regulation. Study Report.

Gan, J., Bondarenko, S., Oki, L., Haver, D. and Li, J.X. 2012. Occurrence of Fipronil and Its Biologically Active Derivatives in Urban Residential Runoff. *Environmental Science and Technology,* 46: 1489-1495.

Goehring, M. 2008. California Department of Pesticide Regulation SOP FSWA014.00: Instructions for the use of the Global FP101 and FP201 flow probe for estimating velocity in wadable streams.

He, Li-Ming. 2008. Study 249 Statewide Urban Pesticide Use and Water Quality Monitoring.

Helsel, D.R., 2012. Statistics for Censored Environmental Data Using Minitab and R (2nd Ed.). John Wiley and Sons. New Jersey.

Oki, L. and D. Haver. 2009. Monitoring pesticides in runoff in northern and southern California neighborhoods.

Jones, D. 1999. California Department of Pesticide Regulation SOP QAQC004.01: Transporting, packaging and shipping samples from the field to the warehouse or laboratory.

Luo, Y., Deng, X., Budd, R., Starner, K., and M. Ensminger. 2013. Methodology for prioritizing pesticides for surface water monitoring in agricultural and urban areas: Analysis memo.

Luo, Y, M. Ensminger, R. Budd, D. Wang, X. Deng. 2017. Methodology for prioritizing areas of interest for surface water monitoring in urban receiving waters of California.

R Core Team, 2014. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.

Segawa, R. 1995. California Department of Pesticide Regulation SOP QAQC001.00: Chemistry Laboratory Quality Control.

Sisneroz, J., Q. Xiao, L.R. Oki, B.J. Pitton, D.L. Haver, T. J. Majcherek, R.L. Mazalewski, and M. Ensminger. 2012**.** Automated sampling of storm runoff from residential areas.

SWAMP. 2017. SPoT: Stream Pollution Trends Monitoring Program. Trends in chemical contamination, toxicity and land use in California watersheds.

Weston, D.P., R.L. Holmes, J. You, and M.J. Lydy. 2005. Aquatic toxicity due to residential use of Pyrethroid Insecticides. *Environmental Science and Technology*, 39:9778-9784.

Weston, D.P., R.L. Holmes, and M.J. Lydy. 2009. Residential runoff as a source of Pyrethroid pesticides to urban creeks. *Environmental Pollution*, 157:287-294.

Weston, D.P and M. J. Lydy. 2014. Toxicity of the insecticide fipronil and its degradates to benthic macroinvertebrates of urban streams. *Environmental Science and Technology* 48:1290-1297.

Table 1. Summary of urban pesticide monitoring locations in Southern California.

County	Watershed	Stormdrain Outfall	Receiving Water/ Mitigation Outfall	Total Sites
Los Angeles	Ballona Creek	-	1	1
Los Angeles	Bouquet Creek	-	1	1
Los Angeles	Los Angeles River	2	1	3
Los Angeles	San Gabriel River	-	1	1
Los Angeles	Dominguez Channel	-	1	1
Los Angeles	Compton Creek	1	-	1
Orange	Anaheim-Barber City Channel	-	1	1
Orange	Bolsa Chica Channel		1	1
Orange	Salt Creek	4	2	6
Orange	Wood Creek	2	1	3
Orange	Peters Canyon Channel (Exploratory Site)	1	-	1
San Diego	San Diego River	1	1	2
San Diego	Chollas Creek	-	1	1
	Total	**11**	**12**	**23**

Table 2. Ambient surface water and mitigation sampling schedule. Subject to change

Site	August Dry	First Storm	Second Storm	June Dry
BOQ	LC, PY6	LC, PY6, DN, PX	LC, PY6, DN, PX	LC, PY6
LAR1	LC, PY6, DN, PX	LC, PY6	LC, PY6	LC, PY6, DN, PX
LAR3	LC, PY6			
LAR4	LC, PY6			
BAL	LC, PY6, DN, PX	LC, PY6	LC, PY6	LC, PY6, DN, PX
SGR	LC, PY6			LC, PY6
DC		LC, PY6		LC, PY6
CC1		LC, PY6		
ABCC	LC, PY6	LC, PY6, DN, PX	LC, PY6	
BCC		LC, PY6	LC, PY6, DN, PX	
PCC1	LC, PY6		LC, PY6	LC, PY6
SC1	LC, PY6	LC, PY6	LC, PY6	LC, PY6
SC2	LC, PY6	LC, PY6	LC, PY6	LC, PY6
SC3	LC, PY6, DN, PX	LC, PY6, DN, PX	LC, PY6, DN, PX	LC, PY6, DN, PX
SC4	LC, PY6	LC, PY6	LC, PY6	LC, PY6
SC5	LC, PY6, DN, PX	LC, PY6	LC, PY6, DN, PX	LC, PY6
SC7	LC, PY6	LC, PY6, DN, PX	LC, PY6	LC, PY6, DN, PX
WC1	LC, PY6	LC, PY6	LC, PY6	LC, PY6
WC2	LC, PY6	LC, PY6	LC, PY6	LC, PY6
WC3	PY6	PY6	PY6	PY6
SDR1	LC, PY6	LC, PY6		LC, PY6
SDR4	LC, PY6	LC, PY6		LC, PY6
CHO		LC, PY6		

*Pesticides includes in screens detailed in Appendix 4. DN=dinitroanline, LC = Liquid chromatography, PX=phenoxy, PY=pyrethroid.
**QC=quality control. Screens will rotate by event.
^Exploratory Sites

Table 3. Toxicity sampling schedule.

Site	Test Species	August Dry	June Dry	First Storm	Second Storm
LAR, BOQ, SC3, SC5, SDR, BAL, SGR, LAR3, PCC1*	*Hyalella azteca*	7	7	7	7
LAR, BOQ, SC3, SC5, SDR, BAL, SGR, LAR3, PCC1*	*Chironomus sp.*	7	7	7	7

*Sites will be rotated for each sampling event

Table 4. Modifications from sampling plan for fiscal year 2019–2020.

Change from FY 19-20	Justification
Adding additional toxicity tests	Collaborative monitoring efforts with SPoT program
Adding PCC1	Adding a drainage location in Peters Canyon Channel in Orange County that receives runoff from commercial land-use to evaluate potential contribution to pesticide loading

Table 5. Non-parametric procedures frequently used for comparing paired data, two samples and three or more samples.

Data	Non-Parametric Procedure
Paired data	*Wilcoxon signed-rank test* for uncensored data *Sign test* (modified for ties) for censored data with one reporting limit *Score tests* for censored data with multiple RLs (the PPW test and the Akritas test)
Two samples	*Wilcoxon rank-sum (or Mann-Whitney) test* or *Kolmogorov-Smirnov test* for censored data with one reporting limit *Score tests* for censored data with multiple reporting limits (the *Gehan test* and generalized *Wilcoxon test*)
Three or more samples in one-way layout	*Kruskal-Wallis test* (for unordered alternative) or *Jonckheere-Terpstra test* (for ordered alternative) for censored data with one reporting limits *Generalized Wilcoxon score test* for censored data with multiple reporting limits *Multiple comparison* to detect which group is different
Three or more samples in two-way layout	*Friedman's test* (for unordered alternative) or *Page's test* (for ordered alternative) for censored data with one reporting limits Multiple comparison to detect which group is different

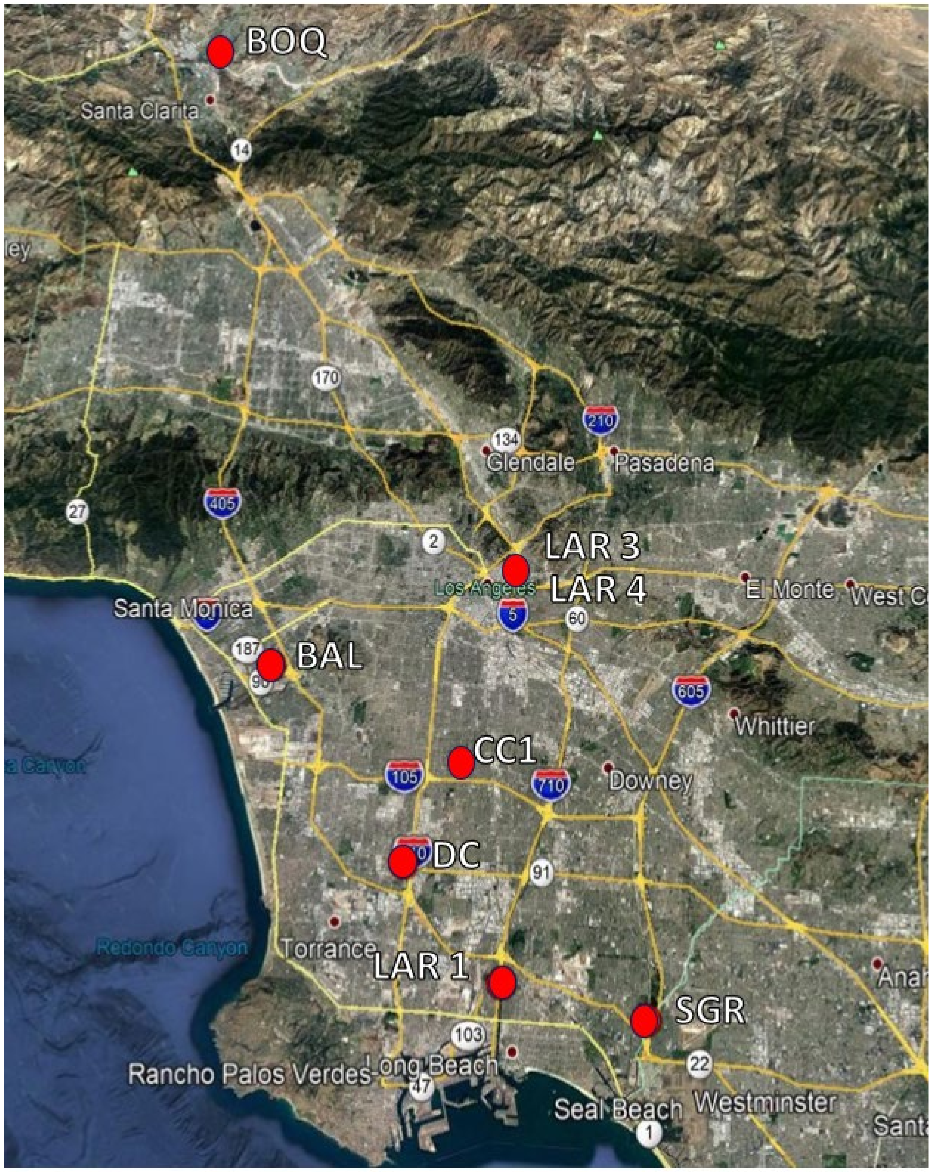

Figure 1. Sampling locations within Los Angeles County, CA.

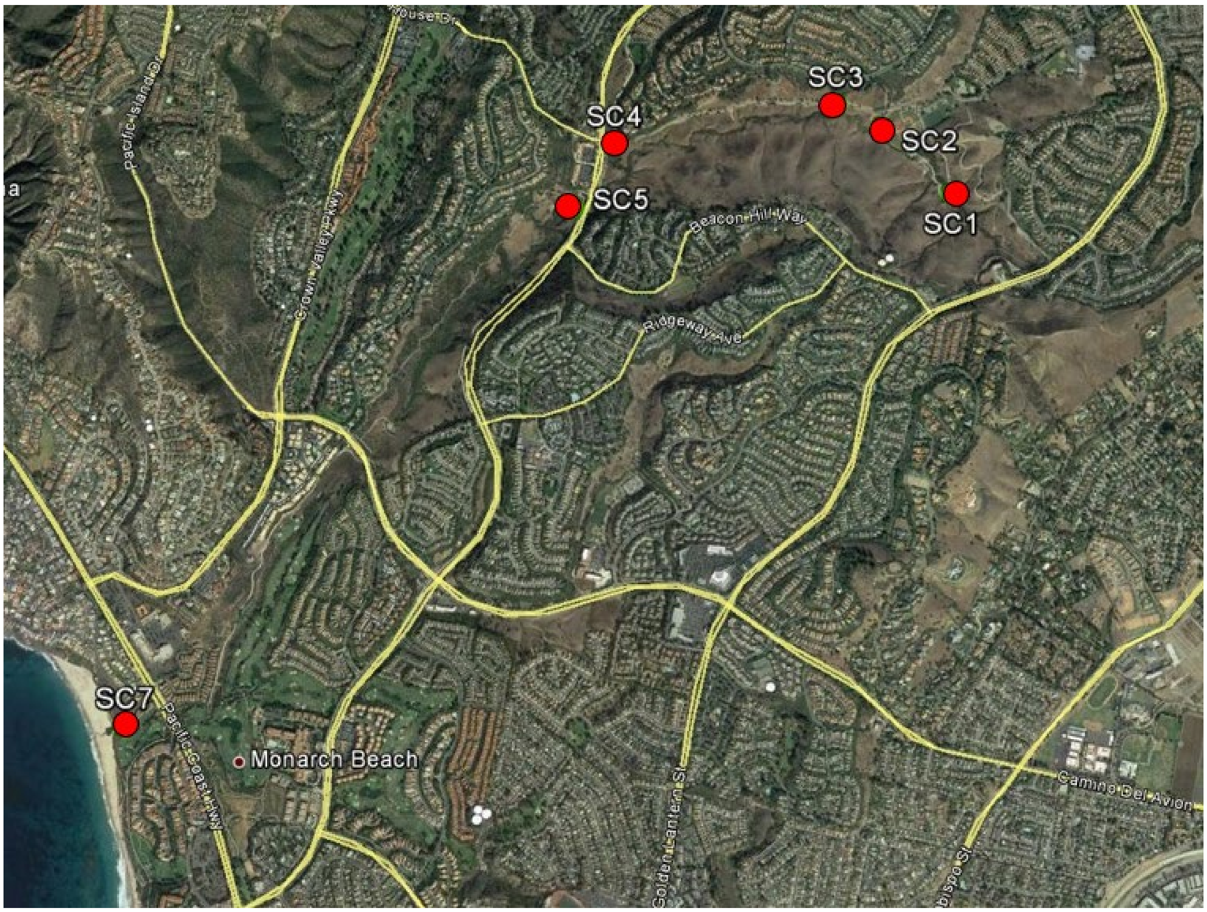

Figure 2. Sampling locations within Salt Creek Watershed, Orange County, CA.

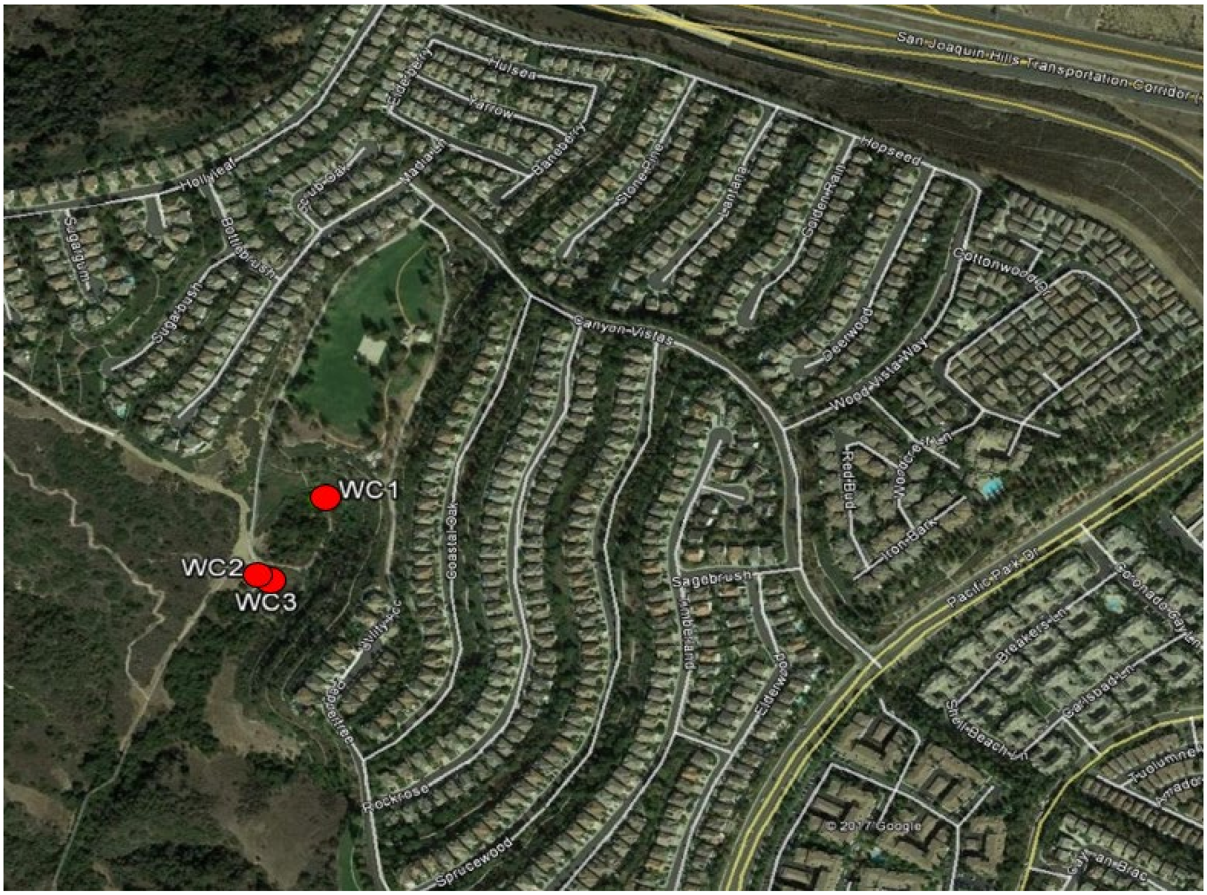

Figure 3. Sampling locations within Wood Creek Watershed, Orange County, CA.

Figure 4. Sampling location with Anaheim-Barber City Channel, Bolsa-Chica Channel, and Peters Canyon Channel in Orange County, CA.

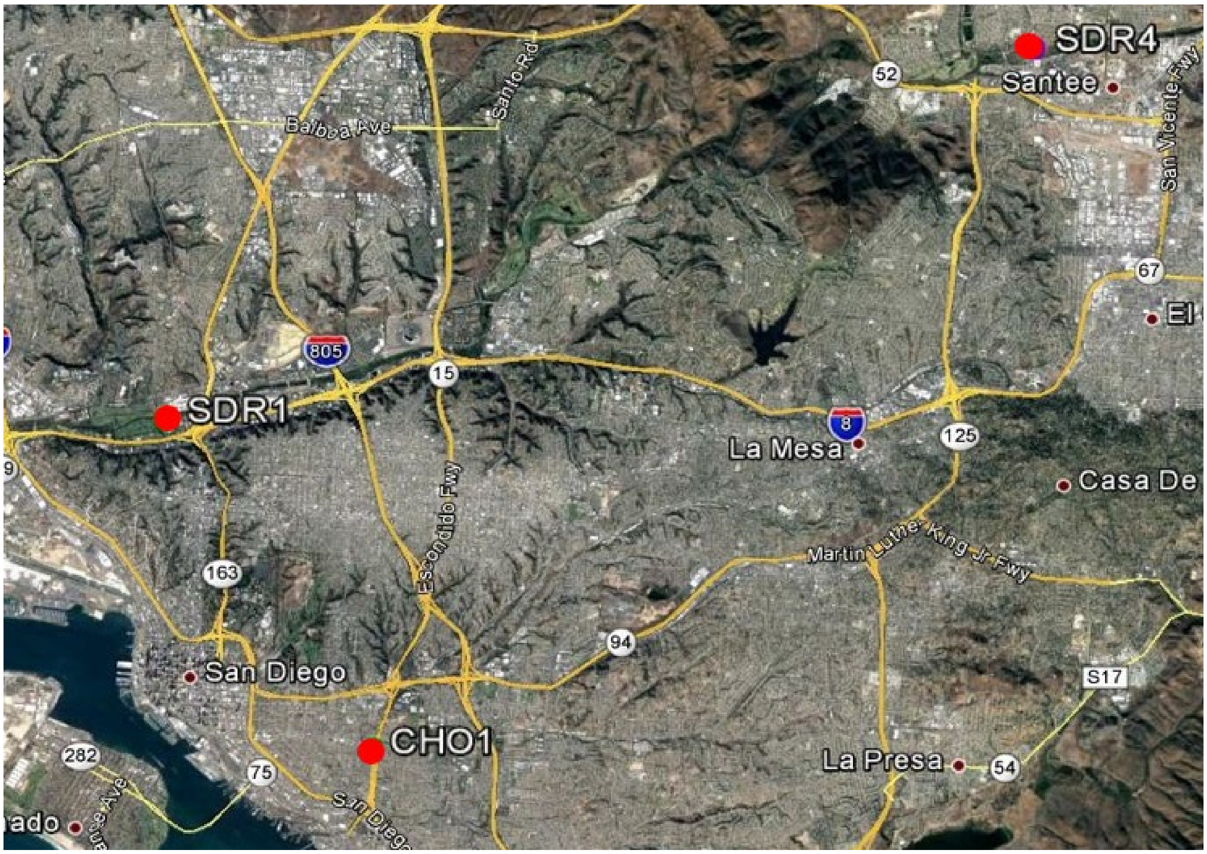

Figure 5. Sampling locations within San Diego County, CA.

Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program
1001 I Street
Sacramento, CA 95812

Appendix 1.

Table 1. Top ten HUC8's identified for urban monitoring in Southern California, ordered by the ranking process.

HUC8 Code	HUC8 Name	CDPR Monitoring Location	Comments
18070201	Seal Beach (Anaheim Bay)	ABCC, BCC	
18070105	Los Angeles	LAR1, LAR3, LAR4, CC1	
18070204	Newport Bay	PCC1	SWAMP location, NPDES permit monitoring at several locations along San Diego Creek*
18070104	Santa Monica Bay	BAL	
18070106	San Gabriel	SGR, DC	
18070203	Santa Ana		Southern California Bight Project monitoring site at base of Santa Ana River*
18070304	San Diego	SDR1, SDR4, CHO1	
18070202	San Jacinto		SWAMP monitoring location along Santa Margarita River*
18070301	Aliso-San Onofre	SC1, SC2, SC3, SC4, SC5, SC7, WC1, WC2, WC3	
18080303	San Luis Rey-Escondido		SWAMP monitoring location along San Luis River*

*Non-CDPR monitoring locations evaluated using California Environmental Data Exchange Network (CEDEN) available at: http://www.ceden.org/

Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program
1001 I Street
Sacramento, CA 95812

Appendix 2.

Table 1. Detailed sampling site information

Watershed	Site ID	Northing	Easting	Site type
Salt Creek	SC1	33.3032.92	-117.4126.53	Stormdrain
Salt Creek	SC2	33.3040.57	-117.4140.67	Stormdrain
Salt Creek	SC3	33.3043.02	-117.4149.55	Stormdrain
Salt Creek	SC4	33.3031.00	-117.4226.34	Stormdrain
Salt Creek	SC5	33.3020.23	-117.4230.87	Receiving water
Salt Creek	SC7	33.2853.97	-117.4326.55	Receiving water
Ballona Creek	BAL	33.5912.92	-118.2455.90	Receiving water
Bouquet Creek	BOQ	34.2542.05	-118.3223.45	Receiving water
Los Angeles River	LAR1	33.8058.09	-118.2054.53	Receiving water
Los Angeles River	LAR3	34.0385676	118.228332	Storm Drain
Los Angeles River	LAR4	34.0385676	118.228332	Storm Drain
Compton Creek	CC1	33.93540	-118.25479	Storm Drain
San Gabriel River	SGR	33.7751.08	-118.0974.18	Receiving water
Dominguez Channel	DC	33.8710.5	-118.2905 69	Receiving water
Anaheim-Barber City Channel	ABCC	33.750297	-118.042183	Receiving water
Bolsa Chica Channel	BCC	33.750261	-118.042493	Receiving water
Peters Canyon Channel	PCC1	33.690339	-117.824827	Stormdrain
San Diego River	SDR4	32.8450.37	-116.9912 06	Stormdrain
San Diego River	SDR1	32.4551.79	-117.1012.24	Receiving water
Chollas Creek	CHO1	32.704850	-117.121143	Receiving water
Wood Creek	WC1	33.3456.56	-117.4443.02	Stormdrain
Wood Creek	WC2	33.5815.83	-117.7457.72	Wetland outfall
Wood Creek	WC3	33.5815.7	-117.7457.27	Stormdrain

Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program
1001 I Street
Sacramento, CA 95812

Appendix 3.

Priority model pesticides (Final Score≥9) based on acute aquatic benchmarks and 2016–2018 urban pesticide usage in Los Angeles, Orange, and San Diego counties, California. All pesticides recommended to monitor based on physical-chemical properties. All pesticides are either within current analytical screens or are undergoing method development.

Table 1. Priority Model Pesticides

Pesticide Name	Pesticide Class	Use (lbs)	Use Score	Acute Benchmark (ppb)	Toxicity Score	Final Score	Analytical Screen
Bifenthrin	Pyrethroid	16669	5	0.07	6	30	Pyrethroid
Permethrin	Pyrethroid	15320	5	0.01	6	30	Pyrethroid
Lambda-Cyhalothrin	Pyrethroid	4729	4	3.50E-03	7	28	Pyrethroid
Imidacloprid	Neonicotinoid	18788	5	0.38	5	25	LC Multi-Residue Screen
Fipronil	Phenylpyrazole	18005	5	0.11	5	25	LC Multi-Residue Screen
Cyfluthrin	Pyrethroid	10486	4	0.01	6	24	Pyrethroid
Deltamethrin	Pyrethroid	2980	3	0.05	6	18	Pyrethroid
Esfenvalerate	Pyrethroid	1379	3	0.02	6	18	Pyrethroid
Chlorfenapyr	Pyrrole	7791	4	2.91	4	16	Dinitroaniline
Prodiamine	Dinitroaniline	3727	4	6.5	4	16	Dinitroaniline
Pyriproxyfen	Pyridine	3036	3	0.18	5	15	LC Multi-Residue Screen
Cypermethrin	Pyrethroid	2492	3	0.19	5	15	Pyrethroid
Carbaryl	Carbamate	1008	3	0.85	5	15	LC Multi-Residue Screen
Oryzalin	Dinitroaniline	4704	4	13	3	12	LC Multi-Residue Screen
Triclopyr, Butoxethyl ester	Pyridine	4397	4	100	3	12	Phenoxy
Propiconazole	Triazole	3640	4	21	3	12	LC Multi-Residue Screen
Oxadiazon	Oxadiazole	1878	3	5.2	4	12	LC Multi-Residue Screen
Pendimethalin	Dinitroaniline	1856	3	5.2	4	12	Dinitroaniline

Pesticide Name	Pesticide Class	Use (lbs)	Use Score	Acute Benchmark (ppb)	Toxicity Score	Final Score	Analytical Screen
Chlorantraniliprole	Anthranilic diamide	793	3	4.9	4	12	LC Multi-Residue Screen
DDVP	Organophosphate	722	2	0.03	6	12	In development for the LC Multi-Residue Screen
Malathion	Organophosphate	407	2	0.05	6	12	LC Multi-Residue Screen
Chlorpyrifos	Organophosphate	125	2	0.05	6	12	LC Multi-Residue Screen
Sulfometuron-methyl	Urea	432	2	0.45	5	10	In development for the LC Multi-Residue Screen
Dithiopyr	Pyridine	2201	3	20	3	9	In development for the LC Multi-Residue Screen
PCNB	Chlorophenyl	2116	3	50	3	9	N/A
Dichlobenil	Nitrile	1958	3	30	3	9	N/A
Indoxacarb	Oxadiazine	1763	3	84	3	9	LC Multi-Residue Screen
Tebuthiuron	Urea	1571	3	50	3	9	LC Multi-Residue Screen
Azoxystrobin	Methoxy-acrylate	1186	3	49	3	9	LC Multi-Residue Screen
Thiamethoxam	Neonicotinoid	866	3	17.5	3	9	LC Multi-Residue Screen

Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program
1001 I Street
Sacramento, CA 95812

Appendix 4.

The following tables show the analytical method reporting levels and method detection limits for pesticides analyzed within screens.

Table 1. LC Multi-Residue Screen: EMON-SM-05-037

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Acetamiprid	Neonicotinoid	0.002	0.02
Azoxystrobin	Methoxy-acrylate	0.0012	0.02
Bromacil	Uracil	0.000977	0.02
Carbaryl	Carbamate	0.011	0.02
Chlorantraniliprole	Anthranilic diamide	0.00182	0.02
Chlorpyrifos	Organophosphate	0.00123	0.02
Desulfinyl fipronil	Phenylpyrazole	0.0011	0.01
Desulfinyl fipronil amide	Phenylpyrazole	0.00244	0.01
Diuron	Substituted urea	0.00116	0.02
Fipronil	Phenylpyrazole	0.000864	0.01
Fipronil amide	Phenylpyrazole	0.00157	0.01
Fipronil sulfide	Phenylpyrazole	0.00111	0.01
Fipronil sulfone	Phenylpyrazole	0.000732	0.01
Imidacloprid	Phenylpyrazole	0.00135	0.01
Indoxacarb	Oxadiazine	0.00066	0.02
Isoxaben	Benzamide	0.0014	0.02
Malathion	Organophosphate	0.00103	0.02
Oryzalin	Dinitroaniline	0.0035	0.02
Oxadiazinon	Oxadiazole	0.00071	0.02
Propiconazole	Triazole	0.00142	0.02

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Pyraclostrobin	Methoxy-carbamate	0.000535	0.02
Pyriproxyfen	Pyridine	0.00114	0.015
Tebuthiuron	Urea	0.003	0.02
Thiamethoxam	Neonicotinoid	0.001	0.02

Table 2. Dinitroaniline Screen: EMON-SM-05-006

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Oxyfluorfen	Dinitroaniline	0.01	0.05
Pendimethalin	Dinitroaniline	0.012	0.05
Prodiamine	Dinitroaniline	0.012	0.05
Trifluralin	Dinitroaniline	0.014	0.05
Chlorfenapyr	Pyrrole		

Table 3. Phenoxy Screen: EMON-SM-05-012

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
2,4-D	Phenoxy	0.015	0.05
Dicamba	Benzoic acid	0.017	0.05
MCPA	Phenoxy	0.022	0.05
Triclopyr	Pyridine	0.02	0.05

Table 4. Pyrethroid Screen: EMON-SM-05-022

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Bifenthrin	Pyrethroid	0.00091	0.001
Cyfluthrin	Pyrethroid	0.00146	0.002
Cypermethrin	Pyrethroid	0.00154	0.005
Deltamethrin/Tralomethrin	Pyrethroid	0.00177	0.005
Fenvalerate/Esfenvalerate	Pyrethroid	0.00166	0.005

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Lambda-cyhalothrin	Pyrethroid	0.00174	0.002
Permethrin cis	Pyrethroid	0.00105	0.002
Permethrin trans	Pyrethroid	0.00105	0.005

Table 5. Sediment Pyrethroid Screen: EMON-SM-52-9

Pesticide	Pesticide Class	Method Detection Limit (µg/kg)	Reporting Limit (µg/kg)
Bifenthrin	Pyrethroid	0.108	1
Cyfluthrin	Pyrethroid	0.183	1
Cypermethrin	Pyrethroid	0.107	1
Deltamethrin/Tralomethrin	Pyrethroid	0.0661	1
Fenvalerate/Esfenvalerate	Pyrethroid	0.0661	1
Lambda-cyhalothrin	Pyrethroid	0.115	1
Permethrin cis	Pyrethroid	0.116	1
Permethrin trans	Pyrethroid	0.135	1

*Full analytical methods are available at: **Analytical Method Page on CDPR Website**